

PATENT SPECIFICATION

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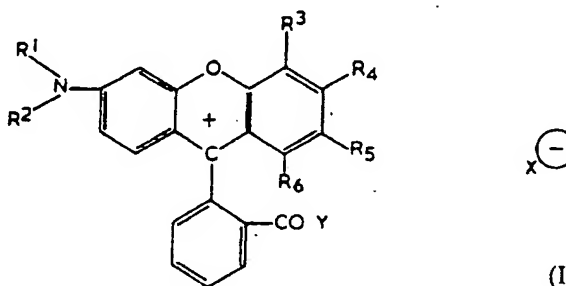


(54) COLOURATION PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the colouration of synthetic polymeric materials in particular polymeric materials comprising polymers and copolymers of acrylonitrile by the application thereto of a certain class of dyestuffs of the fluoran series.

Thus according to the present invention there is provided a process for the colouration of synthetic polymeric materials in particular polymers or copolymers of acrylonitrile which comprises applying thereto a dyestuff of the general Formula I



wherein R¹ is hydrogen or an optionally substituted alkyl group, R² is an optionally substituted aryl group, preferably optionally substituted phenyl, R³, R⁴ and R⁶ are independently chosen from hydrogen, optionally substituted alkyl, aralkyl or aryl groups, acyl, alkoxy, aryloxy, halogen, cyano, nitro, or a group of the formula —COOR⁷, CONR⁸R⁹, —SO₂NR¹⁰R¹¹, or NR¹⁰R¹¹ wherein R⁷ is optionally substituted lower alkyl, R⁸ and R⁹ are independently hydrogen or optionally substituted lower alkyl or aryl, or together form a heterocyclic ring with the amide nitrogen atom, R¹⁰ is hydrogen or optionally substituted lower alkyl, aralkyl, aryl or acyl, R¹¹ is aryl or R¹⁰ and R¹¹ taken together may form a heterocyclic ring with the nitrogen atom the ring optionally containing further hetero atoms, R⁴ may be the same as R³, R⁵ or R⁶ except that when R⁴ is —NR¹⁰R¹¹, R¹⁰ may be hydrogen, lower alkyl, aralkyl, aryl or acyl and R¹¹ may be aryl or with R¹⁰ may form a heterocyclic ring together with the nitrogen atom, or if R¹⁰ is not acyl, R¹¹ may be acyl, Y is O-lower alkyl or —NR¹²R¹³ where R¹² and R¹³ are independently optionally substituted alkyl or aryl groups, or can form a heterocyclic ring with the amide N atom and when Y is —NR¹²R¹³, R⁴ can be the same as R³, R⁵ and R⁶ in all respects, and X is an anion.

Examples of R¹ include hydrogen, methyl, ethyl, propyl, and n-butyl. R¹ is preferably hydrogen or lower alkyl, i.e. an alkyl group containing from 1 to 4 carbon atoms.

Examples of R² include phenyl, 1,3,5-trimethylphenyl, *o*-, *m*- or *p*-chlorophenyl, *o*-, *m*- or *p*-tolyl.

Examples of R³, R⁴, R⁵ and R⁶ include hydrogen, methyl, benzyl, phenyl,

acetyl, benzoyl, methoxy, ethoxy, phenoxy, chlorine, bromine, cyano, nitro, ethoxycarbonyl, carbo-N,N-diethylamide, sulphon-N,N-diethylamide, diethylamino, ethylamino, amino, acetylamino, benzylamino, dibenzylamino, anilino, N-methylanilino, p-toluidino, morpholino, piperidino and pyridin-1-yl.

Examples of R⁷ include methyl, ethyl, propyl, isopropyl, n-butyl and tert.-butyl and benzyl.

Examples of R⁸ and R⁹ include hydrogen, methyl, ethyl, and when taken together with the N atom piperidinyl and morpholinyl.

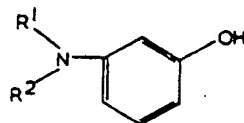
Examples of R¹⁰ include methyl, ethyl, propyl and n-butyl, and where R¹⁰ and R¹¹ are taken together with the N atom, examples include piperidinyl and morpholinyl. Phenyl and o-chlorophenyl are examples of R¹¹.

Examples of Y includes methoxy, ethoxy, phenoxy, benzyloxy, dimethylamino and diethylamino.

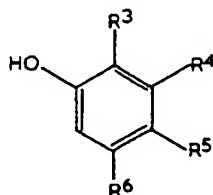
By the term lower alkyl is meant an alkyl group with from one to four carbon atoms.

Examples of the anion X include chloride, bromide, iodide tetrachlorozincate, bisulphate, nitrate, bisulphate, sulphate, sulphamate, phosphate or borate or organic anions such as acetate, propionate, acetate, methosulphate, methylsulphate and p-tolylsulphonate. In those cases where the anion is polyvalent the dyestuffs will contain a corresponding molar proportion of the cationic part of the dyestuff.

The dyestuffs used in the present invention may be obtained by known methods for example by condensation of phthalic anhydride or a substituted derivative thereof with the appropriate optionally substituted meta-aminophenol of the general formula



wherein R¹ and R² are as hereinbefore defined, followed by condensation of the product with a compound of the formula



wherein R³ to R⁶ are as hereinbefore defined, followed by conversion of the carboxylic acid group to a group —COY and solubilisation by salt formation. Dyestuffs of this type have been described in the art.

Colouration of the polymeric material may be carried out by applying the dyestuff from aqueous solution.

The polymeric materials may be for example in the form of tapes, fibres, films, threads or textile materials generally.

The colouration process of the present invention may be applied to polymeric materials generally including polyamides and polyesters, in particular acid modified polyamides and polyesters but is considered especially valuable for application to the dyeing or printing of polyacrylonitrile and copolymers containing acrylonitrile residues. Blends of different polymeric materials either synthetic or natural may also be used.

The colouration process may be carried out by applying the dyestuff from acid, neutral or slightly alkaline aqueous dyebaths, i.e. at a pH of from 3 to 8, at temperatures between 40°C and 120°C preferably between 80°C and 120°C or by printing techniques. Printing techniques which may be used include the known methods in which the usual thickeners and optional printing aids are added and

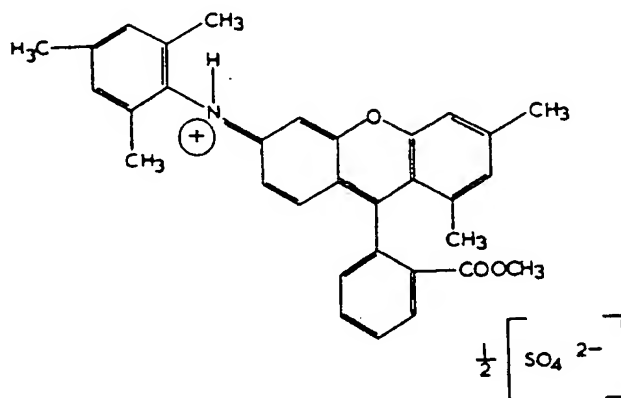
final fixation of the dyestuff takes place in the usual manner, for example by steaming.

The dyeings give bright shades of excellent fastness to light, washing and heat treatment.

The invention is illustrated by the following examples in which all parts and percentages are by weight except where otherwise stated.

Example 1.

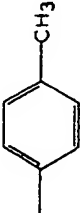
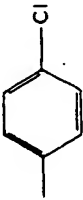
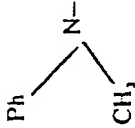
100 Parts of polyacrylonitrile fibre are immersed in 3000 parts of water containing 1 part of a dyestuff of formula:—

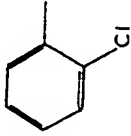
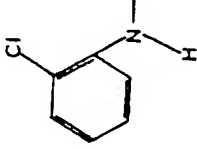
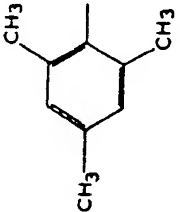

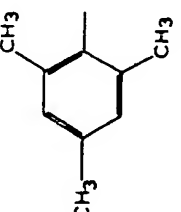



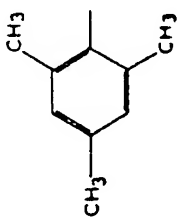

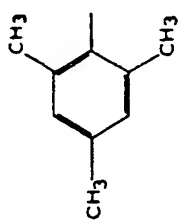

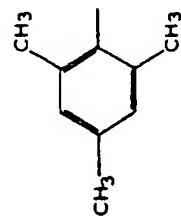


1 part of sodium acetate and 0.6 parts of acetic acid at 60°. The temperature is raised slowly to 100°C, and dyeing continued at this temperature for 90 minutes. The resulting dyeing has a reddish-yellow shade and good fastness to light, washing and heat treatment.

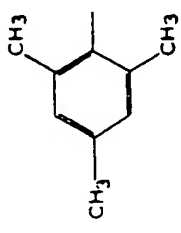
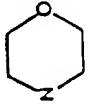
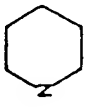
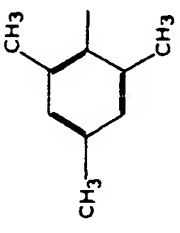
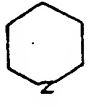
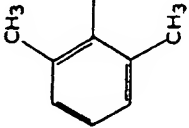
Examples 2—29

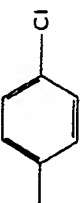
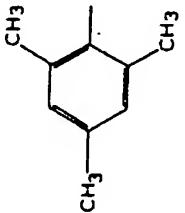
Examples 2—29 are further examples of dyestuffs of Formula I which can be applied in the process of the present invention by the method of Example 1. The substituents are tabulated below and the table includes the shades obtained when the dyestuffs are applied to a polyacrylonitrile textile material.

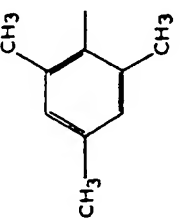
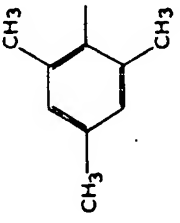
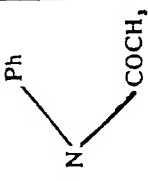
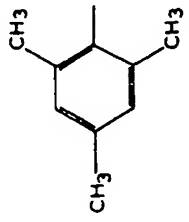
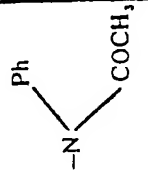
Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Y	X ⁻	Shade on poly-acrylonitrile
2	H	Ph	H	CH ₃	Cl	H	OCH ₃	Cl ⁻	Red
3	H	Ph	H	H	NO ₂	H	OCH ₃	$\frac{1}{2}[\text{SO}_3^{2-}]$	Reddish-yellow
4	H	Ph	Cl	H	Cl	H	OC ₂ H ₅	Cl ⁻	Red
5	CH ₃	Ph	Cl	H	Cl	H	OC ₂ H ₅	Cl ⁻	Bluish-red
6	CH ₃		Cl	H	Cl	H	OC ₂ H ₅	Cl ⁻	Bluish-red
7	CH ₃		Cl	H	Cl	H	OC ₂ H ₅	Cl ⁻	Bluish-red
8	CH ₃	Ph	CH ₃	H	CH ₃	H	NEt ₃	CH ₃ COO ⁻	Red
9	CH ₃	Ph	H		H	H	OCH ₃	Cl ⁻	Blue

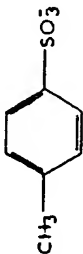
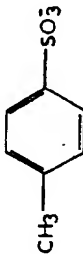

Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Y	X ⁻	Shade on poly-acrylonitrile
10	H		H		H	H	OCH ₃	$\frac{1}{2}(\text{SO}_4^{2-})$	Scarlet
11	H		H	H	NHEt	H		Cl ⁻	Blue-grey
12	H		H	H	NEt ₃	H		Cl ⁻	Dull green

Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
13	H		H	H	$N(CH_2C_6H_4)_2$	H		Cl^-	Dull green
14	H		H	H	$NHCOCH_3$	H		Cl^-	Bluish-red
15	H		H	H		H		Cl^-	Dull green

Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Y	X ⁻	Shade on poly-acrylonitrile
16	H		H	H		H		Cl ⁻	Black
17	H		H	H	NHPh	H		Cl ⁻	Black
18	CH ₃		H	CH ₃	H	CH ₃	N(CH ₃) ₂	CH ₃ COO ⁻	Orange

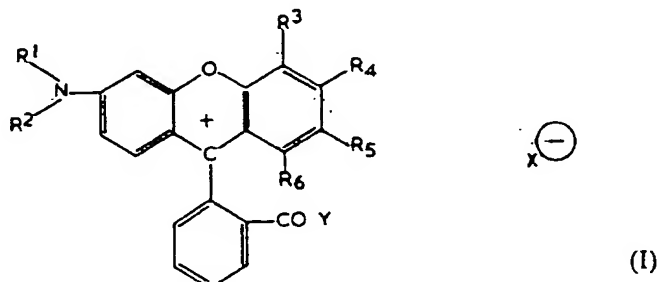
Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Y	X ⁻	Shade on poly-acrylonitrile
19	C ₂ H ₅	Ph	H	CH ₃	H	CH ₃	N(CH ₃) ₂	CH ₃ COO ⁻	Bluish-red
20	n-C ₇ H ₇	Ph	H	CH ₃	H	CH ₃	N(CH ₃) ₂	CH ₃ COO ⁻	Bluish-red
21	CH ₃		H	CH ₃	H	CH ₃	N(CH ₃) ₂	CH ₃ COO ⁻	Bluish-red
22	H		NH ₂	H	CH ₃	H	N(CH ₃) ₂	Br ⁻	Red

Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Y	X ⁻	Shade on poly-acrylonitrile
23	H		H	CH ₃	NH ₂	H	H	N(CH ₃) ₂	Cl ⁻	Rubine
24	H		H	H		H	H	OCH ₃	Cl ⁻	Red
25	ClH ₁		H	H		H	H	OCH ₃	CH ₃ COO ⁻	Bluish-red

Example	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	Y	X ⁻	Shade on poly-acrylonitrile
26	H	Ph	H	H	Br	H	OCH ₃		Red
27	H	Ph	H	CH ₃	N(CH ₃) ₂	H	OCH ₃		Dark red
28	H	Ph	H	OCH ₃	H	OCH ₃	OCH ₃		Red
29	C ₂ H ₅	Ph	H	Cl	H	Cl	OPh	Cl ⁻	Red

WHAT WE CLAIM IS:—

1. A process for the colouration of synthetic polymeric materials which comprises applying thereto a dyestuff of the general Formula I



wherein R¹ is hydrogen or an optionally substituted alkyl group, R² is an optionally substituted aryl group, R³, R⁴ and R⁶ are independently chosen from hydrogen, optionally substituted alkyl, aralkyl or aryl groups, acyl, alkoxy, aryloxy, halogen, cyano, nitro, or a group of the formula —COOR⁷, CONR⁸R⁹, —SO₂NR⁸R⁹ or NR¹⁰R¹¹ wherein R⁷ is optionally substituted lower alkyl, R⁸ and R⁹ are independently hydrogen or optionally substituted lower alkyl or aryl, or together form a heterocyclic ring with the amide nitrogen atom, R¹⁰ is hydrogen or optionally substituted lower alkyl, aralkyl, aryl or acyl, R¹¹ is aryl or R¹⁰ and R¹¹ taken together may form a heterocyclic ring with the nitrogen atom the ring optionally containing further hetero atoms, R⁴ may be the same as R³, R⁵ or R⁶ except that when R⁴ is —NR¹⁰R¹¹, R¹⁰ may be hydrogen, lower alkyl, aralkyl, aryl or acyl and R¹¹ may be aryl or with R¹⁰ may form a heterocyclic ring together with the nitrogen atom, or if R¹⁰ is not acyl, R¹¹ may be acyl, Y is O-lower alkyl or NR¹²R¹³ where R¹² and R¹³ are independently optionally substituted alkyl or aryl groups, or can form a heterocyclic ring with the amide N atom and when Y is NR¹²R¹³, R⁴ can be the same as R³, R⁵ and R⁶ in all respects, and X is an anion.

2. A process as claimed in Claim 1 wherein R¹ is hydrogen or lower alkyl.

3. A process as claimed in Claim 1 or Claim 2 wherein the dyestuff is applied to a polymeric material from aqueous solution.

4. A process as claimed in any one of the preceding claims wherein the polymeric material is polyacrylonitrile or a copolymer containing acrylonitrile residues.

5. A process as claimed in any one of the preceding claims wherein the dyestuff is applied from an acid, neutral or slightly alkaline aqueous bath at a pH of from 3 to 8 at a temperature between 40° and 120°C.

6. A process as claimed in Claim 5 wherein the temperature is from 80° to 120°C.

7. A process as claimed in any one of the preceding claims wherein the dyestuff is applied by a printing technique.

8. A process according to Claim 1 with reference to any one of Examples 1 to 29.

9. Polymeric materials whenever coloured by a process as hereinbefore described and claimed.

DONALD LEES,
Agent for the Applicants.